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U.S. DEPARTMENT OF COMMERCE  
National Bureau of Standards  
Center for Materials Science  
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Washington, DC 20234

Second Annual Report

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U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, *Secretary*  
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director*



# PREDICTION OF THE LONG TERM STABILITY OF POLYESTER-BASED RECORDING MEDIA

by

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## Abstract

The stability of poly(ethylene terephthalate) is being studied in order to predict its long term behavior as the base for film and magnetic tape. This report contains results of the second year's work. Film base, photographic film, and electrographic film are being aged at several temperatures and relative humidities, RH. Acid contents, mechanical properties, and molecular weight have been measured at intervals. The rate of increase in acid content,  $k$ , provides a useful measure of the degradation rate. Data for films aged between 115 and 55 C at 100 % RH obey the equation  $\ln k = 39.3 - (14000/T)$ , where  $k$  is in %/day and  $T$  is the absolute temperature. The water content is included in  $k$ , which is approximately proportional to RH. Lifetimes of the films appear to be equal to  $69.3/k$  days. Extrapolation to 25 and 20 C gives 400 and 900 years for the lifetime at 100 % RH. A more sensitive analytical method than now used will be required to make useful measurements of acid content at 35 C, even after samples have been aged for five years. Two films have always failed before the others. The short-lived films might well be stored with others, since failure of the former would warn of the approaching failure of the latter.

Magnetic tapes are also being aged, primarily to study the binder that holds the magnetic oxide to the substrate. Binder on five brands of tape that were aged at 60 C became crosslinked at RH of zero and 11 %, changed little at 30 % RH, but degraded at 100 % RH. The binder on tapes aged at 85 C and 100 % RH first degraded severely and then appeared to crosslink slightly. Badly degraded binder was not gummy but was easily detached from the substrate. Model binder aged at 85 C and 100 % RH eventually became brittle.

Key words: degradation; hydrolysis; lifetime; magnetic tape; photographic film; poly(ethylene terephthalate); stability

## 1.0 Introduction

Data of many kinds are recorded and stored on photographic film and magnetic tape. Both media contain an active element in a dispersing medium bonded to a substrate consisting of poly(ethylene terephthalate), PET. A PET-based electrographic film is now available which can be revised. The lifetime of the PET under common storage conditions is very long but not known. The lifetime of the dispersing medium for the iron oxide particles of magnetic tapes is also uncertain but is expected to be less than that of PET because the medium is based on polyester polyurethane, which is known to be hydrolytically unstable. For these reasons, the National Archives is sponsoring an environmental aging study of PET and magnetic tapes at the National Bureau of Standards. This is the second annual report in what is expected to be a study lasting five years.

The results with PET in the first year were consistent with the literature. Hydrolytic degradation was the most important process. About 100 days aging at 85 C and 100 % relative humidity, RH, made PET weak and brittle and reduced its molecular weight from about 24000 to 12000. Aging for up to about 150 days at 0, 25, and 50 % RH at 85 C and at 100 % RH at 55 and 35 C caused almost negligible changes in tensile strength, elongation, and molecular weight. About one chain scission per molecule or  $5 \times 10^{-5}$  mol scissions per gram brought about embrittlement, but the imprecision in these quantities was about 50 %. Thus, although PET appeared extremely sensitive to changes in molecular weight, such measurements were not a practical way of measuring the very small amounts of degradation necessary to assess changes at 55 and 35 C or those under ambient conditions.

Acid content is another possible measure of degradation, since each hydrolysis reaction generates an acid group when it breaks the polymer chain. We had procured a potentiometric titrator, in order to measure acid content, but had not had an opportunity to use it before the first report.

Polyester polyurethanes were known to be susceptible to hydrolysis, so this was expected to be the reaction that determined tape lifetime. Our own studies with magnetic tape had not been started at the time of writing the first report. It had been reported that the degradation of the polyester polyurethane binder, which holds the magnetic particles, was limited

by the equilibrium between hydrolysis and esterification and it was concluded that tapes stored at 18 C and 40 % RH should retain acceptable properties indefinitely because of this [1]. We equilibrated polyesters and two polyester polyurethanes at various RH and concluded that hydrolytic equilibrium did not prevent serious loss of properties [2]. However, tape binder differs from the polymers that we studied in that it is highly crosslinked and so may behave differently.

In the second year of work agings have been continued and additional data of the same kind obtained. Acid content was evaluated as a means of measuring degradation of PET. Commercial magnetic tapes were aged and are being evaluated as in reference [1].

## 2.0 Experimental

PET samples included coated and uncoated electrographic film, exposed and developed photographic film, and uncoated film base, all commercially available. Most of these materials were provided by the National Archives but we purchased the film base. We were also given amorphous PET. Some of this was crystallized and some was stretched uniaxially without crystallizing it. Experiments with the latter two samples should give us some knowledge of the effect of crystallinity and orientation on hydrolysis.

Samples of PET were aged in closed containers above water or solutions of LiCl at temperatures of 85, 70, 55, and 35 C and RH of 100, 50, and 25 %. At intervals tensile strength and elongation were measured on a tensile testing machine and molecular weight was measured by gel permeation chromatography, as described in the previous report. Other agings were done in boiling water.

Acid content was measured by potentiometric titration with tetrabutyl ammonium hydroxide in ethanol as base. The polymer was dissolved in a mixture of o-cresol and chloroform. The titrator adds increments of base when the rate of change in the voltage has decreased to some preset value. The end point is reached when the difference between the voltages at successive increments first exceeds and then drops below some preset value. The measurement is precise to about  $2 \times 10^{-6}$  mol acid. This method was used because it is being considered as a standard for the PET base of photographic film certified for archival use.

Ten rolls each of six brands of magnetic tape were purchased. Rolls contain 750 feet of tape except for one set of 2000 foot rolls. All tapes

are 1/2 inch wide and are certified for 6250 bpi. Tapes were the most expensive that the suppliers offered except for the 2000 foot rolls, for which the more expensive and less expensive grades are both being tested. The tapes are being aged at temperatures of 85, 60, and 37 C and RH of 0, 11, 30, and 100 %.

Model tape binder was made in order to explore effects in the absence of the magnetic particles. A commercial polyester polyurethane was dissolved in tetrahydrofuran. Enough toluene diisocyanate was added to react with each urethane group. The tetrahydrofuran was evaporated and the mixture was heated at 100 C for five days. The resulting crosslinked film was extracted with tetrahydrofuran. The sol content was less than 1 %. Samples were aged at 100, 50, and 25 % RH at 85 C.

Magnetic iron oxide was procured and added to a tetrahydrofuran solution of the same polyester polyurethane as above. The tetrahydrofuran was vaporized and the sample was aged at 100 % RH and 85 C for 14 days. Dimethyl formamide was added and the iron oxide was removed by centrifugation. The acid content was then determined.

The weight fraction of binder layer on commercial tapes was determined by immersing about 1.6 g of tape in acetone and then scraping the softened binder and associated oxide off the PET substrate. Then the acetone was evaporated and the dried scrapings weighed. The organic component was then burned off and the residue was weighed, giving the amount of iron oxide. The organic content of the binder layer was taken as the difference between these weights. Soluble portions of the tape were determined by uncoiling about 50 feet into a 4 liter beaker. This was extracted with two 750 cm<sup>3</sup> portions of tetrahydrofuran for a total time of 1 hour. The sol fraction was determined by drying and weighing the tape and by evaporating the filtered solvent to dryness and weighing the residue. Final weighings were made after 60 hours of evacuation. The tapes are quite hygroscopic and weighings were made in closed containers.

The adhesion of the binder layer was tested by applying 3/8 inch-wide sticky tape to the binder layer of unextracted tape and peeling it off in a testing machine. The force required went through an initial maximum and then decreased and became approximately constant during most of the peel. The latter force was taken as the peel strength. The noise level during the peel was about 1/4 to 1/2 as large as the value taken, so the peel strength is not very precisely known. Despite this it should be significant because it varies widely between brands of tape and even between

rolls of the same brand, in the case of one brand. Peel strengths on other brands did not change from roll to roll.

Generally, five 50-foot lengths of a single tape were aged in a closed jar at each temperature and humidity mentioned above. Solutions saturated with LiCl and CaCl<sub>2</sub> gave 11 and 30 % RH. Molecular Sieves were used to get 0 % RH. Individual lengths of tape were removed at intervals and the sol content and peel strength were measured as described above. Tensile strength and elongation were also measured.

### 3.0 Results

#### 3.1 PET.

3.1.1 Preliminary Acid Measurements. The American National Standards Institute Vesicular / Toned Image Task Force ran a round robin using two methods of measuring acid content in PET. We participated in this in order to gain experience with the titrator and the technique. Five samples of PET were analyzed in duplicate by the two methods. All laboratories preferred the method described in the section above. The range of acid contents of the samples was 0.29 to 0.50 X <sup>-4</sup> equiv./g and our values were within that range. A second purpose of the round robin was to measure the effect of the accelerated aging described in ANSI PH1.41-1981 on acid content. All laboratories found no significant effect.

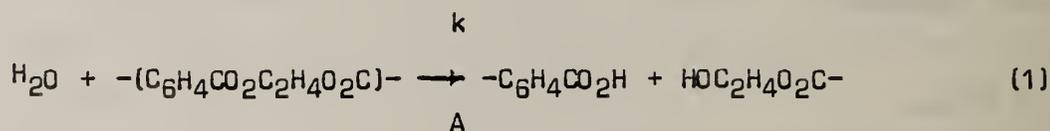
Our laboratory offered to try to find conditions that would offer a more meaningful accelerated aging test. Samples of PET polymers were aged in boiling water and portions were removed at intervals. Tensile strength, TS, elongation, E, and acid content, [A], were measured after the aging was ended. The polymers used were the film base that we used previously and the samples from the round robin that had the highest and lowest acid contents, designated here as E and F. The results obtained are listed in Table I. Values are generally means of two or more determinations.

Acid content increases with aging time. After 17 days the differences between acid contents of the three samples had increased by factors of between three and four. Tensile strength and elongation decrease with aging. About one third of the film base removed as one piece at 14 days broke when it was creased. The remainder, also one piece, did not break when creased. Acid content, tensile strength, and elongation all indicate significant differences between the two portions. The reason for this

behavior is unknown.

Titrations are believed reproducible to about  $2 \times 10^{-6}$  equiv. acid. They were done in duplicate except for sample E at 17 days. The average difference between duplicate determinations was  $2.2 \times 10^{-6}$  equiv. ( $2.4 \times 10^{-6}$  equiv. std. dev.). Portions of polymer used usually contained about  $10^{-4}$  equiv. of acid, so the relative imprecision is about two percent.

Hydrolysis of PET is catalyzed by acid and is autocatalytic because of the acid generated [3]. The reaction is:



Here A represents an acid group and k the rate constant. The water and ester contents change little during the portion of reaction of interest so they can be included in the rate constant. The differential equation connecting [A] and time, t, is  $(d[A]/dt) = k [A]$ , which integrates to  $\ln([A]/[A_0]) = kt$ , where the subscript indicates the initial concentration. Fig 1 is a plot of  $\ln([A]/[A_0])$  versus time. The slope is approximately the same for the three polymers, 8.0 % / day. This represents the rate of increase in acid content.

An initially greater acid content results in greater increases in acid content during aging. Thus the technique makes differences between polymers more obvious. From these data it appears that polymer F originally had a higher acid content than E.

Elongation of film base changes very suddenly between 10 and 14 days aging. One might think of using a ten day aging period in boiling water as an accelerated test and making the criterion of failure be that the acid content not exceed  $10^{-4}$ equiv/g at the end of that period.

3.1.2 PET at 85 C Acid content, number average molecular weight ( $M_n$ ), tensile strength, and elongation for the unaged PET materials are in Table II. The initial range of acid content is 0.31 to  $0.48 \times 10^{-4}$  equiv/g. Aging at 85 C at 100, 50, and 25 % RH increases acid content and reduces tensile strength and elongation, eventually embrittling the material. Data in Table III show these effects for the film base. Samples of aged polymers were small and the imprecision in [A] is about 10 %. "Y" or "N" in the column headed "Crease" indicates whether or not the samples could be

creased without breaking. Elongation must be very low for failure to occur since samples could be creased that had as little as 5 % elongation.

Microfilms A and B, encapsulating film, and coated electrographic film D behaved about the same as film base. Uncoated electrographic film C became brittle much earlier. It failed the crease test at 61 days at 100 % RH, 81 days at 50 % RH, and 341 days at 25 % RH. Coated electrographic film C failed at intermediate times: 81, 146, and 650 days at 100, 50, and 25 % RH, respectively. It is uncertain whether the slightly higher initial acid content of the C films caused their early failure, because there were also initial differences in elongation and heat of fusion, commented on in the first report. Presumably these differences are due to variations in orientation and crystallinity, which could affect the behavior in hostile environments.

Changes in  $M_n$  offer an alternative to acid measurements as a means of calculating the rate constant,  $k$ . Each hydrolytic scission increases the number of acid groups and the number of polymer molecules by one, as shown in reaction 1. Thus the change in the concentration of acid groups,  $[A] - [A_0]$ , is the same as the change in the concentration of polymer molecules,  $\Delta(M_n^{-1})$ , so that  $[A] = [A_0] + \Delta(M_n^{-1})$  and  $\ln \{([A_0] + \Delta(M_n^{-1}))/[A_0]\} = kt$ . Values of  $k$  were calculated from this expression and from  $\ln([A]/[A_0]) = kt$  by assuming a linear variation of the logarithmic quantities with time and using the method of least squares to calculate the slopes, designated  $k_M$  and  $k_A$ , respectively. They are listed in Table IV. The imprecision indicated is the standard error; where none is given only two points were used to calculate the slope. The averages of the values in each column are listed at the bottom of the table with their standard deviations. Neither  $k$  seems to depend on the particular film used but values of  $k_A$  are somewhat larger than  $k_M$ . Probably this is due to some systematic error in the molecular weights, which were measured by GPC. For practical purposes  $k_M$  and  $k_A$  are treated as the same quantity,  $k$ .

**3.1.3 PET at 115, 70, 55, and 35 C at 100 %RH** A sample left from last year that was aged for 13 days at 115 C and 100 % RH in a sealed glass tube has an acid content of  $7.35 \times 10^{-4}$  equiv/g. The value of  $k_A$  is 22.6 %/day.

Data obtained with film base and microfilm B at 70 C are in Table V. The acid contents of these samples have not yet been determined. Values of  $k_M$  are 0.25 and 0.19 %/day for film base and microfilm B, respectively.

Most of the samples aged at 55 C and 100 %RH have shown no signifi-

cant changes in tensile strength, elongation, or molecular weight in almost two years. However, the elongation of the film base of uncoated C was only 63 %, down significantly from 180%. There has also been a significant change in the acid number of the film base. Duplicate determinations on samples which each had about  $0.8 \times 10^{-4}$  equiv. of acid gave acid contents of  $0.44$  and  $0.43 \times 10^{-4}$  equiv/g after being aged for 586 days. The average value of  $k_A$  is 0.037 %/ day.

No detectable change occurred in the PET in samples aged for two years at 35 C and 100 %RH but the coatings on these films have deteriorated even at 35 C and 25 % RH. The gelatin layer of the microfilms has become sticky and even disappeared immediately above the LiCl solution. Electrographic films D and coated C have discolored. We have no samples of these with images and so can not assess the effect on the legibility.

3.1.4 Lifetime of PET Fig 2 is an Arrhenius plot of the rate constants at 100 % RH. The least squares line is shown. The slope of this line gives an activation energy of 117 kJ/mol or 28 kcal/mol. This value agrees well with 27 kcal/mol that we gave last year and also with the value 29 kcal/mol found by McMahon et al. [4].

The glass transition temperature of PET is about 70 C, so finding that the rate at 55 C falls on the same Arrhenius line as rates above the glass temperature implies that it is valid to extrapolate to still lower temperatures. This was done to give rates at 100 % RH at 35, 25, and 20 C. The lifetime,  $t_L$ , can be estimated from these rates as follows. Data in Tables I and III indicate that the acid content approximately doubles before the tensile strength and elongation deteriorate seriously. Consequently, the lifetime was taken as  $(\ln 2)/k$ , where  $k$  is the fractional rate of change in the acid content. Values of  $t_L$  at the three temperatures above are about 90, 400, and 900 years. Data in Table IV indicate that lifetimes at 50 % RH at the same temperatures should be more than twice as long. The lifetimes agree with those estimated by Adelstein and Mc Crea [5].

It is gratifying that these estimated times are so long but it should be noted that the result is greatly dependent on the value at 55 C. The acid content at 55 C should double before this study ends, which will permit more accurate measurement of  $k$ . It is desirable to get a measurement at 35 C to reduce the extrapolation range. The change in acid content at 35 C should be about 2 % after five years, which will be barely signi-

ficant with the current methods.

3.1.5 Future plans with PET The agings will be continued and the acid content at 55 C will be determined with better precision. It is desirable to measure the acid content with about 10 fold greater precision than now being done, in order to measure k at 35 C. Increasing the sample size would help to some extent, but it is already large and using much more would exhaust even our largest samples fairly quickly. An infrared method has been described [6] that involves exposing PET to sulfur tetrafluoride. This converts acid groups to acid flouride groups. These absorb far enough from the ester carbonyl absorption to appear as a separate peak. We intend to test this method using aged samples with known amounts of acid.

Oriented amorphous PET is being aged at 70 C and 100 % RH. Unfortunately, aging it at 85 C causes crystallization, which we wish to avoid. Crystalline PET is also being aged. Results from both samples should be available in about one year. They should give information about the relative importance of amorphous and crystalline regions in the degradation process.

## 3.2 Magnetic Tapes

3.2.1 Background Magnetic tapes consist of  $\text{Fe}_2\text{O}_3$  particles dispersed in a polyester polyurethane-based binder that is bonded to a PET substrate. Conversations with manufacturers who supply products to tape producers indicate that magnetic tapes are made in the following manner. The oxide is coated with a wetting agent, which may be butoxy ethyl stearate or ethyl stearate. A commercial polyester polyurethane is dissolved in tetrahydrofuran. To this are added the oxide and a multifunctional polymeric isocyanate. The suspension is applied to the substrate and the combination is then heated to remove solvent and bring about reaction between the urethane and isocyanate groups to form allophanate linkages:



Catalysts are used to speed up the reaction and a coupling compound may be used to make the binder adhere to the substrate. The binder is highly crosslinked because of the allophanate reaction.

There are about 10 aliphatic ester linkages between urethane links in the original polyester polyurethane. These are more subject to hydrolysis than the aromatic ester linkages of PET and most polyester polyurethanes degrade to soft non-rubbery materials in 10-15 days at 85 C and 100 % RH. The hydrolysis obeys the same kinetic equations as the PET hydrolysis [7]. Lifetimes under ambient conditions are much longer, but in warm moist environments polyester polyurethanes have been known to fail in three years.

Magnetic tapes usually last longer than this, perhaps because their environment is not very humid, but another factor seems to be involved. Cuddihy [8] showed that the acetone-extractable fraction of tape binder on tapes aged for up to 85 days at 36-75 C increased at 100 and 30 % RH but decreased at 11 and 0 % RH. He attributed the decrease to esterification, the reverse of reaction (1), and predicted that tapes could be stable indefinitely because of the equilibrium between esterification and hydrolysis. Decreasing the temperature at constant RH increased the esterification tendency, leading Bertram and Cuddihy to recommend 18 C and 40 % RH as ideal storage conditions [1]. They found that tapes could be used without problems if the content of extractable was less than twice the initial value. Working with soluble polyesters and polyester polyure-

thanes, we found that acid content at 35 C and 25 %RH changed in 300 days from  $3.5$  to  $3.8 \times 10^{-4}$  equiv/g, implying that equilibrium was near or that the time to reach equilibrium was very long [2]. The molecular weight should equal  $[A]^{-1}$  g/mol so it could be as low as 2700. Speculations were made that the high cross link density of tape binder encouraged esterification or caused the binder to remain as gel despite having many chain ends [2].

Cuddihy worked with only about 1.5 g of tape in his samples and the weight fraction of acetone extractable material ranged from 10 to 80 mg. His data are for one unidentified brand of tape although he notes that other tapes behaved similarly. The use of acetone as an extractant raised the possibility that molecular weight limited the weight of extractables, because acetone does not completely dissolve the polyester polyurethane used to make tape binder. Our measurements with this polyester polyurethane gave 7000 and 28000 for the molecular weights of the acetone-soluble portion and the whole polymer, respectively. For these reasons it was decided to repeat the Cuddihy procedures using tetrahydrofuran to extract 10-15 g samples of several brands of tape.

**3.2.2 Initial Tape Characteristics** Table VI lists the weight percentages of the binder layer (oxide plus associated binder and other organic components) and the sol content of each unaged brand of tape. The peel strength is also given. The last two columns give the weight percentage of organic material in the binder layer and the portion of this organic material that is extractable. These two quantities are dependent on the weight of iron oxides and may be inaccurate if the oxides changed when the organic component was burned off. Tape 1 has a back coat that contains carbon. Soluble components of this are included as "Sol" and it was assumed that the coating was 50 % carbon in calculating the value in the last column. Tape 3 contained an acetone-soluble white crystalline material that appeared as a residue surrounding the fragments of binder layer when the acetone had evaporated. This was not observed with the other tapes. The Sol was determined from the weight loss of the tape except with tape 4. The binder layer fell off this tape as soon as it was immersed in tetrahydrofuran so the sol content was determined by filtering the mixture and evaporating the solvent.

Double listings under Sol give results of duplicate determinations and give some feeling for the imprecision of the measurements. These

duplicates were averaged in calculating the sol as a percentage of the organic component of the binder layer. The amounts of sol and the peel strengths vary widely from tape to tape. A greater than sign means that the binder layer did not peel off. Peel strength of tape 5 varied from reel to reel, accounting for the wide limits listed. Portions taken at 400 foot intervals on one reel each of strongly adhering and weakly adhering binder revealed no samples from which binder was stripped from the former reel and no stripping force greater than 40 N/m from the latter reel. Measurements have not yet been performed on tape 6, which is the more expensive of the two grades of tape purchased from one supplier. Tape 5 is the less expensive of these two grades. The supplier of tapes 5 and 6 is not a manufacturer, but has tapes made to his specifications and sells them under his own label. The other tapes bear manufacturer's labels and were purchased from authorized retailers.

3.2.3 Tapes at 85 C and 100 % RH Table VII gives results obtained by aging four brands of tape at 85 C and 100 % RH. Tensile strength and elongation were seriously affected after 46 days. Tapes 1 and 5 broke during handling. Acid contents of these tapes will be determined. The sol content goes through a maximum. The peel strengths were low but were not measured because the tapes were rather brittle. None of the binders became soft or gummy during aging. Instead they tended to flake off, and it was necessary to determine sol fractions by evaporating the tetrahydrofuran. Ordinary polyester polyurethanes would be very soft after 46 days under these conditions.

3.2.4 Tapes at 60 C Table VIII shows the effect of aging the tapes for 85 days at 60 C at 0, 11, 30, and 100 % RH. Values for the unaged tapes are included. The sol contents show the same trend as Cuddihy's data: decreased sol at 0 and 11 %RH and increased sol at 100 % RH. Aging at 30 % RH caused little change in the sol content. Peel strength decreased to about 2/3 of its original value in tape 1 and to 1/10 of its original value in the other tapes at 100 % RH. Aging at lower RH caused smaller changes in peel strength. Significant loss of peel strength occurs at 30 % RH, which might limit tape lifetime. None of the binders appears to have softened during aging.

Peel strengths have been measured at other times during these agings. Most of the loss of strength occurs in the first 40 days.

Tensile strength and elongation have not yet changed significantly in any sample at 60 C.

3.2.5 Model Studies The model tape binder did not soften when aged for two months at 85 C at any RH. Instead samples became stiffer and that aged at 100 % RH is actually brittle. These results appear consistent with the observation that binder layer on magnetic tapes aged at 60 and 85 C did not soften. It may be that there are reactions in addition to hydrolysis and esterification and that some currently unknown reaction brings about crosslinking.

The sample of the polyester polyurethane that was mixed with magnetic iron oxide and aged at 85 C and 100 % RH formed acid faster than polyester polyurethane without the iron oxide. Thus it appears that tape binder ought to be destabilized by the heavy loading of iron oxide.

3.2.6 Future plans with magnetic tapes The agings will be continued. Results from the agings at 37 C will be obtained within a few months. It is planned to put data on tapes from each supplier and store them at 50 and 100 % RH at 20-25 C. These will be read at intervals. More experiments are planned with model binder polymers.

#### 4.0 Discussion

The findings with PET indicate that the material should be quite stable at ambient conditions provided that the process by which PET is made and the rather specific combination of orientation and crystallinity now given the polymer are not changed. If changes were to be made, some knowledge of their effect on stability would be useful.

One could make use of the fact that coated and uncoated films C lose tensile strength and elongation faster than the other materials. Samples of film C could be stored under the same conditions as films used to store archival information. Our results indicate that uncoated C would fail first, followed by coated C. There would be ample time before the failure of the films containing archival information for it to be copied on fresh material.

The changes in the coatings under relatively mild conditions are somewhat disturbing. The films are exposed to laboratory light for about 1/3 of the time. Deterioration of the coatings is usually worst immediately above the liquid interface. Photographic gelatin has been used for a

very long time and it was our impression that it would be stable at 35 C at low RH.

The studies with tapes are not far enough along for us to have come to any firm conclusions. However, we suspect that other reactions than hydrolysis and esterification play a significant part in the process.

### 5.0 Summary

PET has been aged for about two years. Samples aged at 100 % RH at 85 and 70 C deteriorated relatively rapidly. One particularly labile sample shows loss of tensile strength and elongation after aging at 55 C and 100% RH. Lower RH results in much slower degradation but all PET samples at 25 % RH and 85 C lost most of their tensile strength and elongation within two years. Tensile strength and elongation decreased as acid content increased. An increase in acid content of about  $0.4 \times 10^{-4}$  equiv/g from an initial value of about  $0.3 \times 10^{-4}$  can be tolerated. PET became quite brittle when the acid content exceeded  $10^{-4}$  equiv/g. The relation between acid content and time is  $[A] = [A_0] \exp kt$ . The primary difficulty with using acid content to monitor PET degradation is that the required sample size is inconveniently large. An effort is being made to address this problem.

Various magnetic tapes are being aged at different temperatures and humidities. The tapes are rather different initially, in so far as extractables and peel strength are concerned. Sol contents increase at 100 % RH but decrease at low RH. The binder layer behaves differently from the polyester polyurethane from which it is derived since the former does not seem to soften during aging. The reasons for the difference are unknown.

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TABLE I

Acid Content, Tensile Strength, and Elongation at Break of PET Aged in Boiling Water

Time Days	$10^4$ [A] equiv/g	TS <sup>1</sup> MPa	E %
Film Base (4 mil thick)			
0	0.36	215	142
3	0.45	192	130
5.9	0.55	179	135
9.7	0.73	150	103
14.0	1.05	116	40
14.0	1.15	71	2
17.0	1.41	Weak	Brittle
E (7 mil thick)			
0	0.29	162	90
3	0.36	173	113
5.9	0.45	171	97
17	1.13	95	4
F (4 mil thick)			
0	0.50	--	--
17	1.84	weak	brittle

<sup>1</sup> 1 MPa = 145 PSI.

Table II  
 Properties of Unaged PET<sup>1</sup>

	$10^{-4}$ [A] equiv /g	$10^{-4}$ M <sub>n</sub> g/mol	TS MPa	E %
Film Base	0.35	1.77	204 <sup>2</sup>	144
Microfilm A	0.31	2.15	200	126
Microfilm B	0.32	1.69	193	122
Encapsulating Film	0.37	1.59	177	80
Uncoated Electrographic Film C	0.41	1.44	116	185
Coated Electrographic Film C	0.48	1.54	167	105
Coated Electrographic Film D	0.34	1.68	201	99

<sup>1</sup> 4 mil films except D which is 4.8 mil.

<sup>2</sup> 1 MPa = 145 PSI.

TABLE III

## PET Film Base at 85 C

Time Days	RH %	$10^4$ [A] equiv/g	$10^{-4} M_n$ g/mol	$10^5 \Delta(M_n)^{-1}$ mol/g	TS MPa	E %	Crease Y/N
Unaged	-	0.35	1.77	0	204	144	Y
61	100		1.15	3.0	170	113	Y
76	100	0.64	1.13	3.2			Y
81	100	0.85	1.07	3.7	108	18	Y
97	100	1.25	0.85	6.1	114	5	Y
108	100		0.80	6.9	weak	brittle	N
178	100	5.05	0.55	12.5	weak	brittle	N
97	50		1.19	2.7	158	80	Y
146	50		1.41	1.4	150	100	Y
340	50	1.66	0.68	9.1	weak	brittle	N
154	25		1.77	0	190	142	Y
341	25		1.34	1.8	155	107	Y
650	25				136	78	Y

Table IV. HYDROLYSIS RATE CONSTANTS IN PET FROM ACID CONTENT ( $k_A$ ) and MOLECULAR WEIGHT ( $k_M$ ) at 85 °C

Units of  $k_A$  and  $k_M$  are %/day

Polymer	100% RH		50% RH		25% RH
	$k_A$	$k_M$	$k_A$	$k_M$	$k_M$
Film Base	1.49 ± 0.09	0.92 ± 0.13	0.45	0.36 ± 0.08	0.12
Microfilm A	1.27	1.14 ± 0.08	0.47	0.41 ± 0.02	0.12 ± 0.07
Microfilm B	1.33	1.09 ± 0.01	0.48	0.22 ± 0.01	0.20 ± 0.10
Uncoated C	1.80	0.67	0.68	0.29 ± 0.07	0.16 ± 0.07
Coated C	1.24	1.14 ± 0.12	0.56	0.39 ± 0.04	0.14 ± 0.01
Coated D	1.51 ± 0.06	0.84 ± 0.30	0.56	0.28 ± 0.10	0.21 ± 0.03
Encap. Film	1.02 ± 0.27	1.10 ± 0.08	0.50	0.38 ± 0.04	
Average	1.38 ± .25	1.02 ± 0.19	0.52 ± 0.09	0.33 ± 0.07	0.16 ± 0.04

Table V

PET at 70 C and 100% RH

<u>Material</u>	<u>Time/days</u>	<u><math>10^{-4}M_n/g/mol</math></u>	<u>TS/MPa</u>	<u>E/%</u>
Film Base	0	1.77	204	144
	136	1.41	183	124
	312		117	39
Microfilm B	0	1.69	193	122
	136	1.46	132	75
	312		110	23
(1)	136	1.46	131	65
(1)	312		128	56

(1) Microfilm B aged after removal of the gelatin layer.

Table VI

## Characteristics of Unaged Magnetic Tape

Tape	Binder Layer (BL) wt%	Sol Content wt%	Peel Strength <sup>1</sup> N/m	Organic in BL wt%	Sol in Org BL wt%
1	20 <sup>2</sup>	0.8, 0.9	325	30 <sup>3</sup>	9.5 <sup>4</sup>
2	23	1.4	> 800	24	25
3	32	2.1, 2.6	150	25	30
4	24	4.8	> 800	29	69
5	28	0.7, 0.6	35-→450	26	9.7

<sup>1</sup> 1N/m = 1.02 g/cm

<sup>2</sup> Not including the back coat with carbon black that is 6% of the tape weight

<sup>3</sup> Oxide binder only

<sup>4</sup> Assuming half the back coat is carbon

Table VII  
 Effect of Aging Magnetic Tape at  
 85 C and 100% RH

Time Days	TS MPa	E %	So1 %	So1 in Org BL
Tape 1				
0	230	139	0.8	9.5
18			4.7	56
46	130	5	4.3	51
Tape 2				
0	290	118	1.4	25
18			3.0	55
46	143	40	2.4	44
Tape 3				
0	230	103	2.4	30
18			2.4	30
46	130	32	1.8	23
Tape 5				
0	220	130	0.7	9.7
18			5.0	69
46	115	4	4.1	57

Table VIII  
Effect of Aging Magnetic Tapes at  
60 °C for 85 Days

R.H. %	Sol wt%	Sol in Org BL wt%	Peel Strength <sup>(1)</sup> N/m
Tape 1			
Unaged	0.8	9.5	325
0	0.5	6.0	350
11	0.6	7.1	
30	0.5	6.0	250
100	4.6	55	200
Tape 2			
Unaged	1.4	25	>800
0	0.8	15	>600
11	1.0	18	>650
30	1.3	24	100
100	2.7	49	50
Tape 3			
Unaged	2.4	30	150
0	1.4	18	140
11	1.8	23	
30	2.3	29	60
100	5.4	68	15
Tape 4			
Unaged	4.8	68	>800
0	4.0	56	>700
11	3.5	49	
30	4.4	62	>750
100	5.0	77	25
Tape 5			
Unaged	0.7	9.7	>450
0	0.4	5.5	>500
11	0.3	4.2	
30	0.7	9.7	>400
100	5.3	74	12

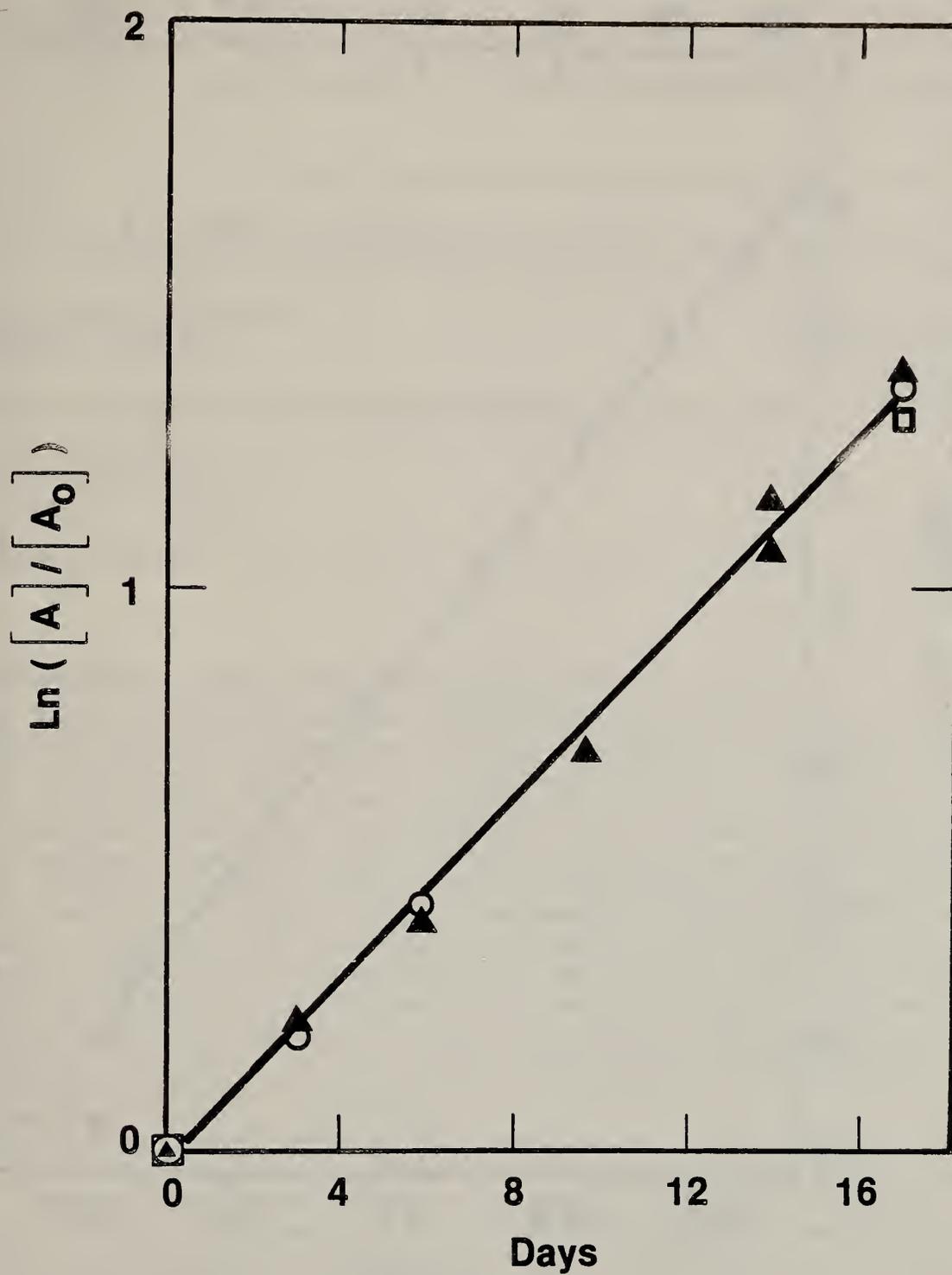


Fig. 1  $\text{Ln}([A]/[A_0])$  vs Aging time in boiling water.

▲, Film base; ○, polymer E; □, polymer F;

—,  $\text{Ln}([A]/[A_0]) = 0.080t - 0.017$

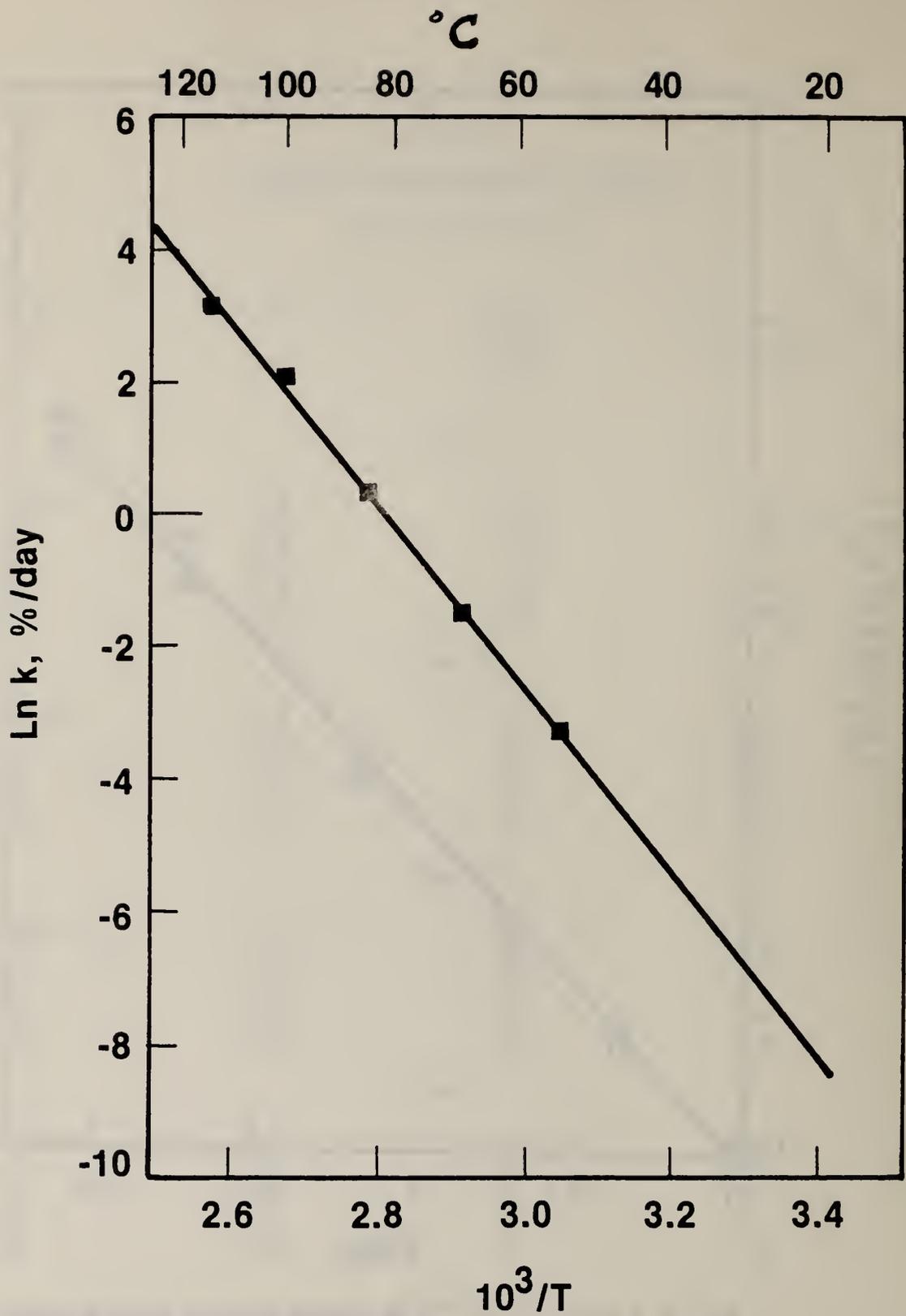


Fig. 2 Arrhenius Plot for PET at 100% RH.  $k_A$  was used when it was available; otherwise,  $k_M$  was used.  
 —,  $\ln k = -(14000/T) + 39.3$

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<p>The stability of poly(ethylene terephthalate) is being studied in order to predict its long term behavior as the base for film and magnetic tape. This report contains results of the second year's work. Film base, photographic film, and electrographic film are being aged at several temperatures and relative humidities, RH. Acid contents, mechanical properties, and molecular weight have been measured at intervals. The rate of increase in acid content, <math>k</math>, provides a useful measure of the degradation rate. Data for films aged between 115 and 55 C at 100 % RH obey the equation <math>\ln k = 39.3 - (14000/T)</math>, where <math>k</math> is in %/day and <math>T</math> is the absolute temperature. The water content is included in <math>k</math>, which is approximately proportional to RH. Lifetimes of the films appear to be equal to <math>69.3/k</math> days. Extrapolation to 25 and 20 C gives 400 and 900 years for the lifetime at 100 % RH. A more sensitive analytical method than now used will be required to make useful measurements of acid content at 35 C, even after samples have been aged for five years. Two films have always failed before the others. The short-lived films might well be stored with others, since failure of the former would warn of the approaching failure of the latter.</p> <p>Magnetic tapes are also being aged, primarily to study the binder that holds the magnetic oxide to the substrate. Binder on five brands of tape that were aged at 60 C became crosslinked at RH of zero and 11 %, changed little at 30 % RH, but degraded at 100 % RH. The binder on tapes aged at 85 C and 100 % RH first degraded severely and then appeared to crosslink slightly. Badly degraded binder was not gummy but was easily detached from the substrate. Model binder aged at 85 C and 100 % RH eventually became brittle.</p>			
<b>Key words:</b> degradation; hydrolysis; Lifetime; magnetic tape; photographic film; poly(ethylene terephthalate); stability			
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